

## Supplemental materials

### 5.0.1 XRD powder measurements

### 5.0.2 Spin–Lattice Relaxation Time $T_1$ .

The spin–lattice relaxation time allows to determine the interaction of the system of nuclear spins with the closest neighborhood. The dependence of spin–lattice relaxation time  $T_1$  vs. reciprocal temperature (see Figure 8 in the Supporting Information section) shows that the cations in both compounds can perform isotropic reorientations below the phase transition temperature therefore are the minor factor which affects the mechanism of PT. The fact that cations rotate freely below phase transition temperature is also suggested by the high values of the activation energy of the rotation releasing,  $E_a$ , found for both studied compounds, which was observed in  $[(\text{CH}_3)_2\text{CHNH}_3]_2[\text{SbBr}_5]$  as well (Jakubas R., Bator G., Ciapała P., Zaleski J., Baran J. and Lefebvre J., *J. Phys.: Condens. Matter*, 1995, 7, 5335). In our case the relaxation time of cation rotations obeys the Arrhenius law:  $\tau_c = \tau_{c0}\exp(E_a/RT)$ . In the case of  $[(\text{CH}_3)_3\text{PH}][\text{SbCl}_4]$  the magnetization was fitted by one exponential function in the whole studied temperature range. In the case of  $[(\text{CH}_3)_3\text{PH}][\text{SbBr}_4]$  the fit with one exponential function was possible below 164 K. Above this temperature the magnetization was well fitted using sum of two exponential functions. The temperature variations of  $T_1$  are shown in Figure 8 for two compounds investigated. The temperature dependencies of spin–lattice relaxation time are quite similar to each other. In the both cases in low temperatures well formed deep minimum is observed at 110 K with  $T_1 = 19$  ms and  $T_1 = 26$  ms for PSbCl and PSbBr, respectively.

In order to quantitatively analyze the obtained data we applied the theory proposed by Albert et al. (Albert S., Gutowsky H. S. and Ripmeester J. A., *J. Chem. Phys.*, 1972, 56, 3672). It provides a model not only for the expected reorientation of the  $\text{CH}_3$  group around  $C_3$  axis (including C–P bond) but also for an independent rotation of the whole trimethylphosphonium cation around  $C_3'$  axis (including the P–H bond). From this theoretical model the separate activations parameters sets are obtained. For simplicity only the intraionic dipolar relaxation is considered. Two correlation times,  $\tau_1$  and  $\tau_2$ , are defined as follows: the first correlation time results from the stochastic  $120^\circ$  jumps of protons in the methyl group and the second one is the result of the rotation of three methyl group around  $C_3'$  axis. This model of reorientations by dipolar interactions between protons of trimethylphosphonium cation is described as:

$$\left(\frac{1}{T_1}\right)_{\text{INTRA}} = \frac{1}{60} \frac{\gamma^4 \hbar^2}{r^6} \left( 8g(\omega_0, \tau_1) + 19g(\omega_0, \tau_3) + 8g(\omega_0, \tau_2) \right) \quad (1)$$

in which  $r$  (1.79 Å) is the interproton distance in the  $\text{CH}_3$  group,  $1/\tau_3 = 1/\tau_1 + 1/\tau_2$  and  $g(\omega_0, \tau) = \frac{\tau}{1+\omega_0^2\tau^2} + \frac{4\tau}{1+4\omega_0^2\tau^2}$  is the spectral density of the correlation function from Bloembergen–Purcell–Pound (BPP) theory (Bloembergen N., Purcell E. M., Pound R. V., *Physical Review*, 1948, 73, 679–746). The dipolar relaxation

time between protons belonging to different adjacent  $\text{CH}_3$  groups within the cation is approximated by:

$$\left(\frac{1}{T_1}\right)_{\text{INTER}} = \frac{27}{20} \frac{\gamma^4 \hbar^2}{R^6} g(\omega_0, \tau_2) \quad (2)$$

where  $R = 3.04$  Å and is the distance between the centres of the  $\text{H}_3$  triangles formed by the three protons of each  $\text{CH}_3$  group. The experimental values are the sum of both interactions and combined equation has the form:

$$\left(\frac{1}{T_1}\right)_{\text{Total}} = \frac{9}{10} \frac{\gamma^4 \hbar^2}{r^6} \left[ \frac{2}{15} g(\omega_0, \tau_1) + \frac{19}{60} g(\omega_0, \tau_3) + \frac{2}{15} g(\omega_0, \tau_2) \right] + \frac{27}{20} \frac{\gamma^4 \hbar^2}{R^6} g(\omega_0, \tau_2) \quad (3)$$

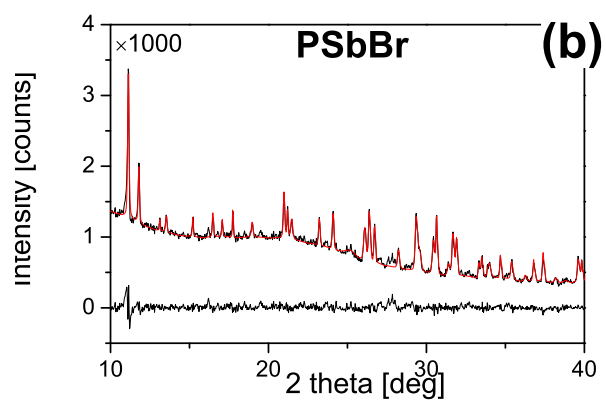
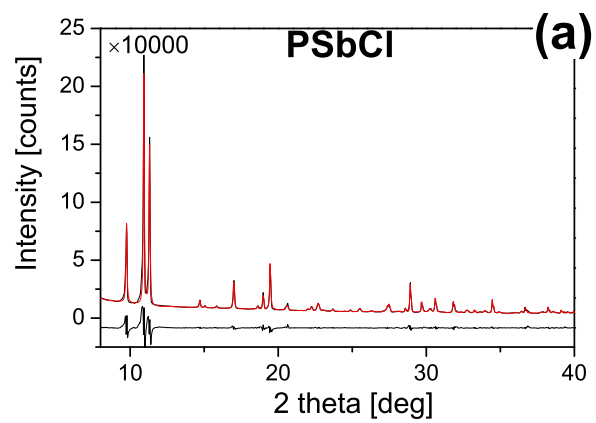
The coefficient 9/10 is applied due to the presence of the additional interaction via fast spin diffusion of all nine protons of the methyl groups with the tenth proton attached directly to phosphor.

In the present experiment the deep  $T_1$  minimum observed for each complex around 110 K may be attributed, according to above theory, to the reorientation of the  $\text{CH}_3$  groups in the trimethylphosphonium cations. The higher temperature minima observed (only parts before phase transition are visible) originate from the reorientation of the whole cation around its  $C_3'$  axis. The parameters of molecular dynamic obtained from numerical fitting procedure are presented in the Table 7.

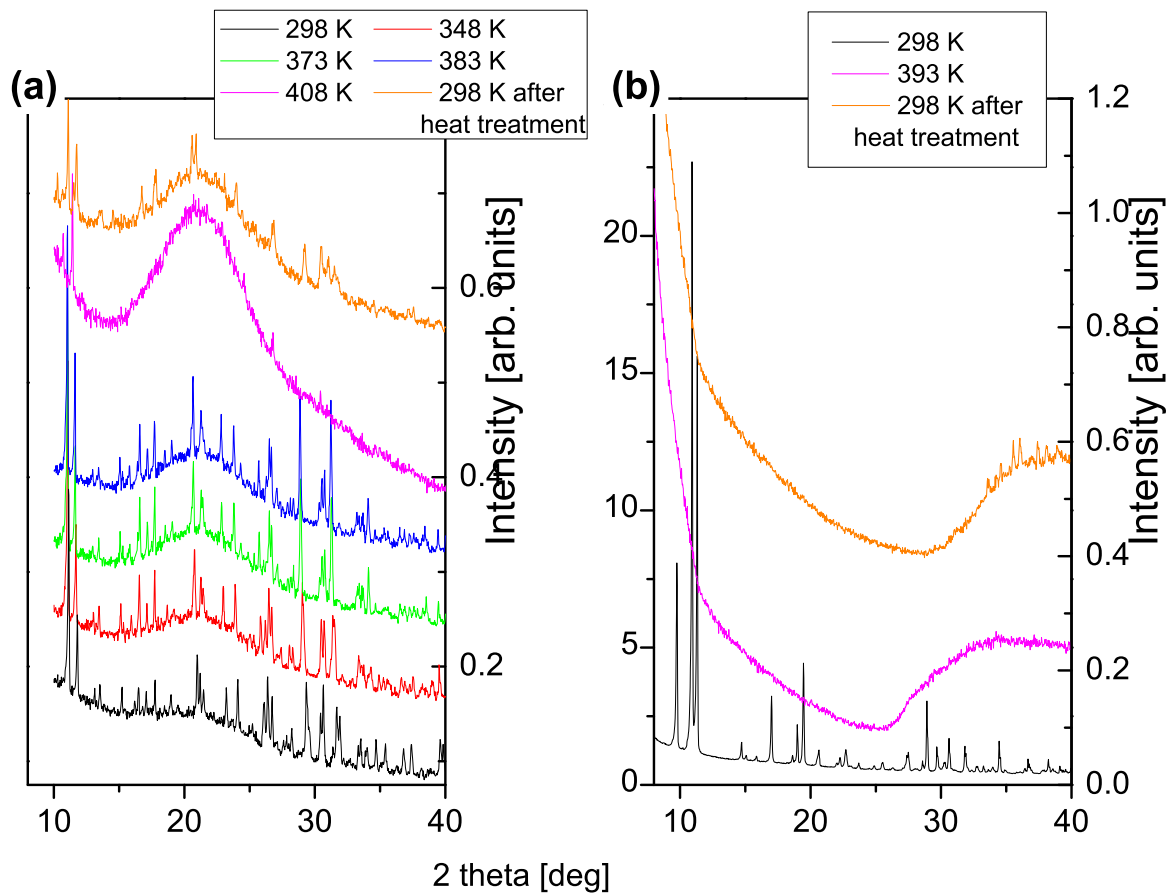
**Table 7** Motional parameters evaluated from the equation 3 for reorientation of trimethylammonium cation in studied compounds.

Parameters	PSbCl	PSbBr
$C_3$ reorientation		
$E_a$ [kcal/mol]	1.8	1.8
$\tau_{0,1}$ [s]	$0.95 \cdot 10^{-12}$	$1.1 \cdot 10^{-12}$
pseudo $C_3'$ reorientation		
$E_a$ [kcal/mol]	3.8	3.6
$\tau_{0,2}$ [s]	$4.1 \cdot 10^{-11}$	$2.7 \cdot 10^{-11}$

The second component of the relaxation time in temperatures above 164 K for  $[(\text{CH}_3)_3\text{PH}][\text{SbBr}_4]$  can be explained by the presence of quadrupolar nuclei of bromine. Such interaction of protons is not observed in the case of  $[(\text{CH}_3)_3\text{PH}][\text{SbCl}_4]$ . This means that the quadrupolar coupling of bromine is distinctly stronger than in the case of the chlorine analog and gives rise to a fast quadrupolar relaxation of those nuclei via additional pathway.



**Fig. 6** The results of the Le-Bail fit (red) of the XRD powder data for PSbCl (a) and PSbBr (b) measured at ambient conditions (black) together with the difference plot.



**Fig. 7** The powder diffractograms measured at high temperatures for PSbBr (a) and PSbCl (b)

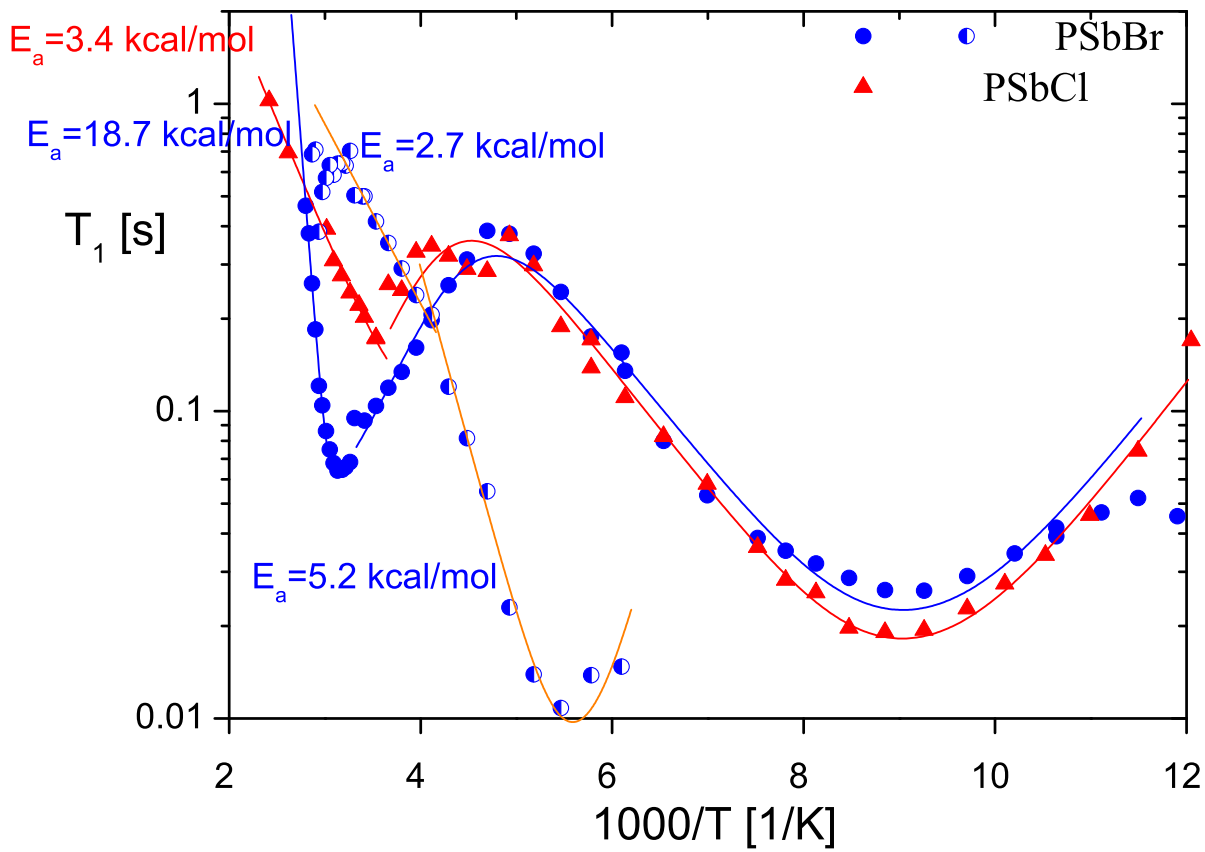


Fig. 8 Spin-lattice relaxation time  $T_1$  vs.  $1000/T$  of PSbCl and PSbBr.